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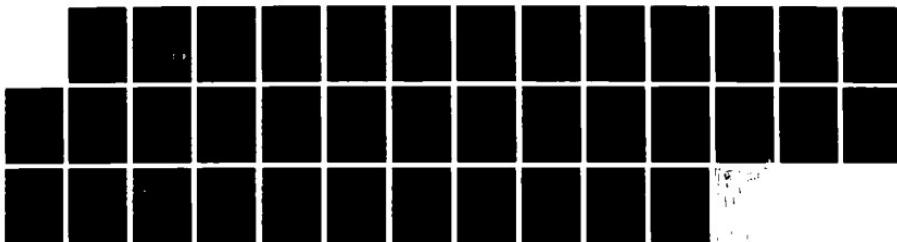
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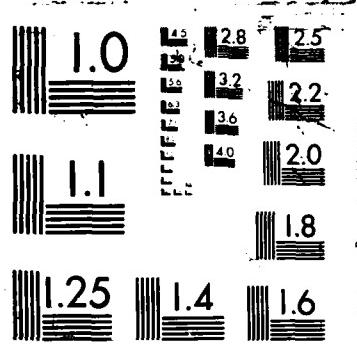
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An Electrochemical and Spectroelectrochemical Study of Substituted  
Alkylidene Cyclopropabzenes: 1-(Diphenylmethylene)Cyclopropabenzene  
in the First Anodic and Cathodic Voltammetric Waves in Acetonitrile

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By

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AN ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL STUDY  
OF SUBSTITUTED ALKYLIDENE CYCLOPROPABENZENES:  
1-(DIPHENYLMETHYLENE)CYCLOPROPABENZENE IN THE  
FIRST ANODIC AND CATHODIC VOLTAMMETRIC WAVES IN ACETONITRILE

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ABSTRACT

Electrochemical and modulated specular reflectance spectroelectrochemical (MSRS) investigations were performed on 1-(diphenylmethylene)cyclopropabenzene in nominally dry acetonitrile solution. The results indicate the formation of a stable anion radical ( $\lambda_{max}^{anion} = 587\text{nm}$ ) and a quasi stable cation radical ( $\lambda_{max}^{+} = 473\text{nm}$ ). The first order homogeneous rate constant for the decay of the cation radical was computed.

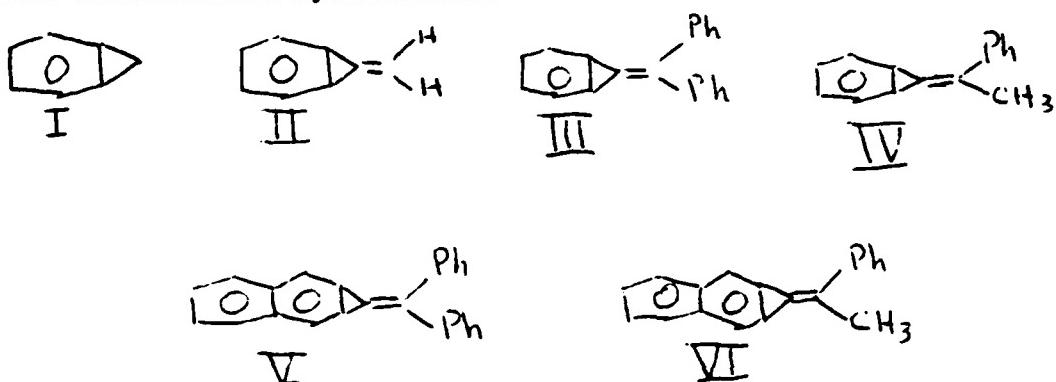
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## INTRODUCTION

The unusual properties and reactivity of highly strained molecules have interested chemists for quite some time (1). Presently there is a great deal of interest and research activity in cycloproparene chemistry. Cycloproparenes possess some of the highest strain energies known (2); the parent compound I has a strain energy of 68 kcal/mol (3). As a result, the electrochemical oxidation and reduction potentials of the neutral molecules are lower than those of most other electroactive hydrocarbons.



Even more highly strained and unusual alkylidene derivatives of I have been reported (4): the 1,1-diphenyl (III) and the 1-methyl-1-phenyl (IV) derivatives have been synthesized, as well as the corresponding naphthalene analogs V and VI. Compounds III and V are stable in air and in aprotic solvents against rapid oxidation. To date, the methylenecycloproparene parent compound II has not been successfully isolated, but attempts to synthesize this species continue.

The possibility of charge separated resonance forms contributing to the stability of the neutral molecule V was suggested by an initial spectral characterization. We have recently reported the results of an electrochemical and spectroelectrochemical study of V (5), and in an effort to further characterize and understand the nature of the special properties of these molecules we have undertaken an electrochemical and spectroelectrochemical

investigation of III. One question is how large a role does the aromatic moiety attached to the cycloproparene ring play in the stability of the ion radicals compared to the substituents on the methylene group. The naphthalene analog in the previous study was shown to form a stable anion radical (on the timescale of the experiment) when electrochemically reduced in oxygen-free acetonitrile solution. When oxygen is present the anion radical reacts rapidly with O<sub>2</sub> at a rate approaching the diffusion limit. Additionally, the compound was shown to form a quasi stable cation radical when electrooxidized. In the present study, compound III has been found to behave similarly. In addition, the homogeneous rate constant for the decay of the cation radical in acetonitrile solution has been computed from spectroelectrochemical transient data.

## EXPERIMENTAL

### Chemicals and Reagents

The preparation of III has been described in detail (4). A stirred solution of cyclopropabenzene in dry THF was cooled to -70°C under oxygen free nitrogen. n-butyllithium in hexane was added slowly, while the bath temperature was allowed to rise to -40°C. After 1.5h the solution was again cooled to -70°C, and trimethylsilyl chloride was added dropwise until the deep orange solution had become colorless. The reaction mixture was allowed to warm slightly for 1h and then cooled again to -70°C, at which time the above metallation procedure with n-butyllithium was repeated. Quenching of the generated  $\alpha$ -silyl carbanion was attained with benzophenone in THF, and the resulting clear yellow solution was allowed to warm to room temperature. After 1.5h aqueous sodium bicarbonate was added after which the mixture was extracted with dichloromethane. The combined organic extracts were washed with water, dried with magnesium sulfate, and

concentrated to an orange oil under reduced pressure. This oil was then passed through a silica gel column (petroleum ether: ethyl acetate, 9:1) and fractions of the most mobile component, 1-(diphenylmethylene)cyclopropabenzene, were collected as a yellow oil which solidified on standing at -20°C. Recrystallization from petroleum ether gave yellow needle-like crystals, m.p. 89-91°C.

The preparation of tetra-n-butylammonium tetrafluoroborate (TBAF) has been described previously (6). This supporting electrolyte was prepared from the metathesis of sodium tetrafluoroborate and tetra-n-butylammonium hydrogen sulfate. The crude product was washed with ice water, dissolved in a minimum amount of methylene chloride, and precipitated with cold diethyl ether. After a second recrystallization, the product was air dried and stored in a vacuum oven at 75°C for 24h before use.

Acetonitrile was HPLC grade (Baker Chemicals, 0.001% nominal water content) and was used as received. Deoxygenation of the reaction mixture was accomplished by purging with dry helium gas immediately prior to the experiments.

The reference electrode was a silver wire immersed in 0.01M silver nitrate and 0.10M TBAF in acetonitrile. We report all potentials with respect to this reference.

#### Electrochemistry and Spectroelectrochemistry

A three electrode potentiostat and a waveform generator (JAS Instrument Systems, Inc.) provided the control of electrode potential. Cyclic voltammetry was conducted in a three-electrode kinetic cell wherein a platinum wire working electrode surrounded by a cylindrical platinum foil secondary electrode was mounted. A Luggin capillary reference electrode tip was situated within about

1mm of the working electrode. Although the geometry of the setup is cylindrical, the experiments were carried out on a timescale where linear diffusion is observed. See (7) for precise details. For spectroelectrochemical experiments, a cell was used that held a 7mm diameter platinum mirror disk working electrode with a planar Pt foil counter electrode situated opposite, providing good linear diffusion characteristics for up to 10 seconds. Two quartz windows were mounted to enable passage of incoming and outgoing UV/VIS radiation at a 45° angle of incidence and reflectance. A Luggin reference probe was positioned close to the working electrode so as not to obstruct the optical path. Exact details have been described previously (8).

The spectroelectrochemical cell was mounted on an optical bench, and radiation from a monochromator (GCA McPherson model 302) was directed onto the electrode surface, and reflected onto a photomultiplier tube (RCA model 31000A). The signal from the PMT was digitized by an oscilloscope (Tektronix model 5223); this data was transmitted over a GPIB interface to a computer (IBM PC/AT). The computer signal averaged digitized data from single reflectance transients; the background intensity was controlled so that the value of the relative reflectance could be calculated as described in (8). The MSRS technique used in this work was implemented by first maintaining the potential at a value where no electrochemical reaction occurred. The potential was then stepped to a value where electrooxidation or electroreduction was forced into diffusion control, and the spectroelectrochemical reflectance transient response of the electrogenerated species was recorded on the digitizing oscilloscope as a function of time after the potential pulse was applied. Alternately, the potential was also modulated at a high frequency (40Hz) and the resulting ac reflectance change monitored with a lock-in amplifier; scanning wavelength simultaneously provided UV-VIS

difference spectra of the reactants, intermediates, and products (8).

## RESULTS AND DISCUSSION

### Voltammetry

#### A. Anions

At a platinum electrode, the reduction of a blank solution containing only supporting electrolyte showed no faradaic current ( $<0.1\mu\text{A cm}^{-2}$ ) over the range of potentials studied. Cyclic voltammetry of III at negative potentials in oxygen-free acetonitrile solution is shown in Figure 1a. A one-electron wave due to the reduction of the neutral molecule to the anion radical at the platinum working electrode is observed. The voltammetric response indicates electrochemical reversibility at this ( $50 \text{ mV s}^{-1}$ ) and faster sweep rates: the voltammetric peak separation is 60mV, and the ratio of cathodic to anodic peak currents is unity. The half-wave potential is -2.32V vs. Ag/Ag<sup>+</sup>. There is no evidence of anion radical decay on the experimental timescale (ca. 1 minute): the anion radical is quite stable, as is that of the naphthyl cycloproparene analog (5).

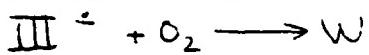
When only oxygen is present in solution a voltammogram such as that in Figure 1b results. The first cathodic wave at -1.60V (vs. Ag/Ag<sup>+</sup>) corresponds to the reduction of oxygen to superoxide, which is a kinetically slow electron transfer (5). On the return excursion an anodic peak at -0.78V due to the reoxidation of superoxide is seen. The diffusion controlled peak for the formation of superoxide is thus 750mV less negative than the peak potential for the formation of the anion radical of III at a sweep rate of 50mV/s. (At glassy carbon the reduction of oxygen is kinetically more reversible: the separation between the cathodic peak due to the formation of superoxide and the corresponding oxidation peak is reduced from about 820mV at platinum to 240mV on

carbon at these sweep rates).

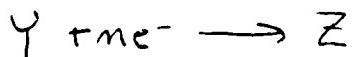
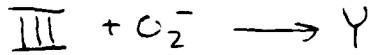
Plots of cathodic peak current versus square root of sweep rate for both dioxygen and isolated III are linear for sweep rates of up to 500mV/s; the plots intersect the origin. This is the expected result for an electrochemical reaction where there are no complicating side reactions occur involving reactants or products, and where there are no complications due to adsorption of species undergoing electron transfer. Uncomplicated electrochemical formation of the anion radical of III and of superoxide is thus consistent with observations; both reductions are simple one-electron transfers.

However, solutions containing both III and oxygen demonstrate more complicated voltammetry than that of the individual systems described above (Figure 2). As in Figure 1, the first reduction wave at -1.60V corresponds to the formation of superoxide. We observe, however, that the magnitude of the current in the second wave at -2.35V, due to the formation of the anion radical of III is larger than that for the simple one electron transfer as was observed in the single component III system. There are several possible explanations for this behavior.

One possibility is the case where an electroactive product is formed whose reduction potential is less negative than that of III. In the situation at hand, this would most likely be due to the reaction of the anion radical of III with diffusing oxygen or superoxide:



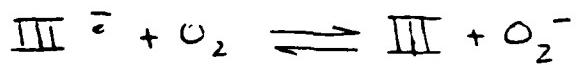
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(The second reaction is unlikely, as it is unfavorable energetically.) However, bulk electrolysis of III at potentials up to and less negative than ~2.35V yielded no evidence of the expected products of either of the proposed reaction schemes. Additionally, if such an electron transfer-chemical step-electron transfer scheme was indeed occurring, the height of the second cathodic wave would imply the involvement of more than one electron in the reduction of W or Y which, though possible, is unlikely.

Voltammetric experiments revealed no evidence of the reaction of unreduced III with oxygen. Upon deoxygenation with helium purging of the mixed (both III and O<sub>2</sub> present) solution, the uncomplicated electrochemical behavior shown in Figure 1a could be reproduced. Also, if in the mixed system, a cyclic voltammogram was run to a switching potential past the peak for oxygen reduction but prior to the cathodic wave corresponding to reduction of III, the reverse sweep yielded an oxidation peak for superoxide which was uncomplicated, as per Figure 1b. This is evidence that superoxide does not react chemically to any appreciable extent with III, although Figure 2 shows a depletion of available total radical anion of III in the diffusion layer; the oxidation peak at -2.29V is reduced in magnitude when O<sub>2</sub> is present. All of the above possibilities suggest that a product of the addition of III and oxygen should be observed, but exhaustive electrolyses at or beyond the second reduction wave gave no significant yields of any product of III save the anion radical.

Another possible explanation for the unusually high current seen in the second reduction wave (in the mixed system) is the catalytic regeneration of III by reaction of oxygen with the anion radical to form III and superoxide:



In turn, superoxide reacts with the anion radical to form III and peroxide in the presence of a proton donor:



These results imply that electrochemical reduction of superoxide to peroxide is thermodynamically feasible at potentials where III is reduced, but that the electrode reaction is very slow. The formation of peroxide in acetonitrile has been previously observed (9), where superoxide in the presence of any available proton donor was reported to disproportionate to peroxide and oxygen. Bulk electrolysis of the mixed system at a potential of -2.40V did indeed give rise to solutions which were found to contain peroxide ion, as evidenced by testing with Fenton's reagent. Thus, if III is regenerated continuously in the presence of oxygen, the cathodic current at the electrode, which is diffusion limited, will be expected to increase as observed, without the production of any other organic product of III (except the anion radical).

Figure 3 shows a plot of the normalized (to the square root of the sweep rate) current magnitude as a function of the sweep rate for the aromatic hydrocarbon-oxygen system. The lowest plot (I) is that for the oxygen reduction peak. Plot (II) is that for the uncomplicated one electron reduction peak of III to its anion radical in the absence of oxygen. Plot (III) is for the cathodic peak at -2.35V when both III and oxygen are present in comparable amounts. The reduction peak in plot III is the sum of the currents for the reduction of III to its anion radical and the reduction of electroactive products formed from the reaction of the anion radical with oxygen and superoxide, which the data suggest to be more regenerated III as proposed in the preceding paragraph.

It should be noted that in the mixed system, a subsequent cathodic excursion

following cyclic voltammetry from 0 to -2.5V vs. Ag/Ag<sup>+</sup> gave rise to no additional reduction waves at lower potentials than that for III reduction. This is further evidence that no long-lived organic products of the reaction of the anion radical with O<sub>2</sub> and superoxide other than III are generated. Though short-lived products of this reaction cannot be ruled out, the fact that the cathodic peak at -2.35V grows in comparison with the anodic peak at -2.29V is certainly consistent with regeneration of additional III.

The half wave potential for the reduction of III is 400 mV more negative than that for the reduction of V (5). This is the expected result in view of the greater delocalization of the extra electron possible in the larger pi orbital system: the stability of the naphthyl anion is greater than that of the benzyl analog, just as it is known to be in naphthalene and benzene. We have performed simple Huckel calculations on III and V and find that this assumption is in line with the results of those calculations.

#### B. Cations

In deoxygenated acetonitrile solution, a voltammetric sweep to positive potentials gives rise to single electron oxidations of III to its radical cation and of its radical cation to dication (Figure 4). The second reduction is irreversible; the lifetime of the dication is very short on the experimental timescale. On the other hand, the anodic and cathodic peak potentials corresponding to oxidation of III and reduction of III<sup>+</sup>, respectively, are separated by 60mV at sweep rates up to 500mV s<sup>-1</sup>, suggesting electrochemical reversibility; the half-wave potential is +0.68V. However, the anodic peak current is much greater than the cathodic peak current, and the ratio of cathodic

to anodic peak current increases with sweep rate (Figure 5). These observations are consistent with a reversible electron transfer followed by slow decomposition of the resulting cation radical, probably by reaction with trace water (5). If the potential is swept immediately to negative values following the oxidation of III to its cation radical, a new peak appears at about -0.7V (Figure 4); this peak is apparently due to the reduction of the decomposition product(s) of the cation radical. If the potential is swept positive enough to form the dication, and then immediately swept negative to potentials where the anion radical is formed, no peak for the reduction of the dication is observed; only the reduction due to the aforementioned cation radical decomposition product shows up. This reaction product was not characterized, but its identification is the subject of continuing work.

At a glassy carbon electrode, virtually identical behavior was observed for III at all applied potentials. Also, oxygen had no effect on the electrochemistry of the cation radical nor dication; the very same voltammetry as described above was observed even if oxygen was present in solution.

It is interesting to note that the half wave potential for the oxidation of the benzyl derivative III is about 130mV less positive than the half wave potential for the oxidation of the naphthyl derivative V (5). This surprising result is not explained by simply considering the stabilities of the ions as was possible in the case of the reduction of these two compounds. The result can be explained for both oxidation and reduction if one assumes that there is a large difference in the ground state energies of the two neutral compounds III and V, and lesser differences in the electronic energies of their respective cation radicals. If neutral V is energetically more stable than III, it will be more difficult to oxidize than III, given that the cations of each are closer in

energy than are the neutral species. This trend was indeed indicated in the Huckel calculations; the overall stabilization energy of V was predicted to be greater than that of III, while the electronic energy difference between the cation radicals was less than the energy difference between the neutral species.

### C. Structural Considerations

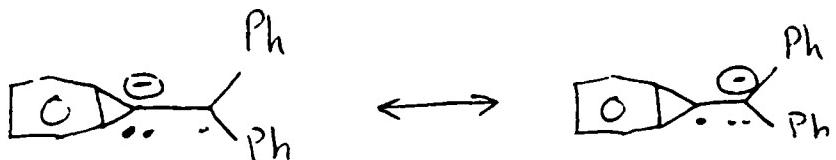
The consideration of the possible structures of the electrochemically formed ion radicals is of interest. The reversible behavior of III upon oxidation and reduction indicates that no opening of the three-membered ring occurs when either the cation radical or the anion radical is formed. The compound is reduced at slightly less negative potentials than many other aromatic hydrocarbons in acetonitrile. The half-wave potential for the reduction of III was seen to be -2.32V vs. Ag/Ag<sup>+</sup>. This value compares with half-wave potentials of -2.9V for naphthalene, -2.5V for tetraphenylethylene, -2.5V for pyrene, -2.4V for diphenylanthracene, and -1.93V for diphenylmethylenecyclopropa(b)naphthalene. Compound III is oxidized at somewhat less positive potentials than many other aromatic hydrocarbons in this solvent. It has a half-wave potential of +0.68V for oxidation to the cation radical. For naphthalene this value is +1.40V, for pyrene +1.06V, for tetraphenylethylene +1.0V, for diphenylanthracene -0.92V, for anthracene +0.91V, for diphenylmethylenecyclopropa(b)naphthalene +0.81V, and for perylene +0.66V.<sup>1</sup>

On formation of the radical ions, it is most likely that the olefinic double bond is broken. This release of strain would yield a reduced free energy of ion formation. The anion would be then formed at less negative potentials and the cation formed at less positive potentials than what might be predicted from half-

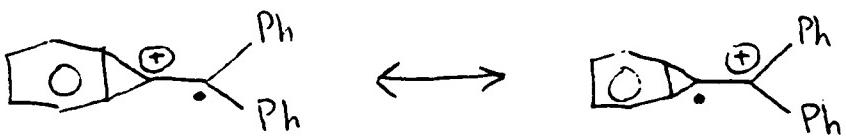
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<sup>1</sup>These half-wave potentials were obtained from references (5), (10) and (11), assuming where necessary that the potential of the Ag/Ag<sup>+</sup> reference electrode is 0.3V more positive than that of the saturated calomel electrode.

wave potentials of other aromatic hydrocarbons. Proposed structures for the anion radical are:



while possible structures for the radical cation might be:



It is not possible from our voltammetric data to conclude for either species which resonance structure contributes most to the lowest overall energy state.

### Spectroelectrochemistry

#### A. The Anion Radical

Modulated specular reflectance spectroscopy (MSRS) in the visible range was performed on solutions containing III in millimolar quantities in acetonitrile in the absence of oxygen. The potential was stepped from 0V to -2.50V and the frequency of modulation was 40Hz. The MSRS technique is described more explicitly in (8) and (12). A single peak ( $\lambda_{\text{max}} = 587\text{nm}$ ) due to absorption by

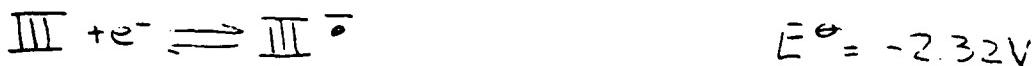
the radical anion was observed. Reflection spectroelectrochemical transients for the formation of the anion radical were then obtained at this wavelength using the same potentials. Figure 6 shows the transient for radical anion formation of III at the platinum mirror electrode in the absence of oxygen. Composite transient data from 100, 200, 400, and 1000ms transients were combined to examine the linearity of the optical response with the square root of time over an extended period. Linearity indicates anion radical stability over the examined timescale, if the amplitude of  $\Delta R/R$  is kept small. The plots of  $-\Delta R/R$  vs.  $t^{1/2}$  were indeed linear with a correlation coefficient of 0.99885, showing the radical anion to be very stable for times of at least 1s. This also demonstrates the reproducibility and accuracy of this transient technique.

Figure 7 shows the transient that results when oxygen is present in solution together with III. MSRS data of this system at the same potentials of modulation still revealed a single peak at the same wavelength as that for the oxygen-free system, demonstrating that superoxide does not absorb at this nor at any nearby frequency. We still observe the formation of the radical anion during the forward potential step although the reflectance is somewhat less. When the potential is reversed to its base value, however, to where only neutral III and  $O_2$  are stable, the reflectance, which is proportional to absorbance at low values of  $\Delta R/R$ , is observed to decay rapidly to zero. Clearly, the anion radical of III reacts rapidly with oxygen.

Regeneration of III is suggested by the observed reflectance-time profile during the forward applied potential pulse; the shape of the transient is still a linear function of the square root of time.  $III^\cdot$  diffuses from the electrode surface into the oxygen and superoxide rich solution, neutral III is formed and can thereafter diffuse back to the electrode and undergo another reduction.

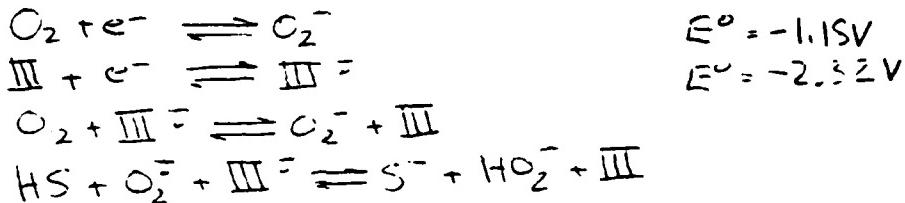
The results are consistent with the following proposed mechanism for the cathodic reduction of III:

IN THE ABSENCE OF OXYGEN



In oxygen-free solution a simple electron transfer occurs reversibly to form the anion radical from neutral III.

IN THE PRESENCE OF OXYGEN



Here the mean of the oxidation and reduction peak potentials for dioxygen have been taken to be the standard potential. During the forward potential step, the rate of production of the anion at the electrode is limited by the diffusion of the neutral species to the surface. Reaction of anion with oxygen and superoxide regenerates the neutral molecule, so more of III is available to diffuse to the interface. In this manner the absorbance of the radical anion in oxygen-containing solution is not much lower than it is in the solution in which oxygen is not present. During the reverse potential pulse, however, the oxygen consumes the anion while the regenerated starting material cannot react electrochemically to form more anion to replace that which is consumed. The reflectance therefore falls rapidly in comparison to the case in an oxygen-free environment.

The supporting electrolyte cation, TBA<sup>+</sup>, probably acts as a proton donor in the proposed scheme. The peroxide dianion most likely abstracts a proton from the background electrolyte. Further studies on this possibility are underway and will appear elsewhere.

Evidence for the greater stability of the anion radical of V than that of III is apparent from the MSRS experiment. The wavelength of maximum absorption for the anion radical of III appears at 587nm, while that for the anion radical of V is observed at 529nm (5); the energy of the electronic transition for the naphthyl derivative anion radical is higher than that for the benzyl derivative anion radical. Energy levels predicted from the Huckel calculations appeared at relative energies which are consistent with this data.

#### B. The Cation Radical

An MSRS spectrum was obtained as before for the cation radical formation from III, by stepping the electrode potential from 0V to +0.9V, which causes diffusion controlled mass transport of neutral III to the electrode. The wavelength of maximum  $\Delta R/R$  was found at 473nm for the formation of the radical cation. Identical spectra resulted whether O<sub>2</sub> was present or absent in the solution. Spectroelectrochemical transients for the anodic oxidation of III to its radical cation were then taken at the above  $\lambda_{max}$  for pulse lengths of 20, 40, 100, 200, and 400ms duration; a typical transient is shown in Figure 8. Such transients were identical whether O<sub>2</sub> existed in solution or did not, suggesting no cation radical reaction with oxygen. The composite data from the above transients of different length were plotted as before ( $\Delta R/R$  vs.  $t^{\frac{1}{2}}$ ) (Figure 9). The plot is linear up to times of about 100ms, and thereafter we see a fall-off region; the cation radical is stable for a short period before it undergoes

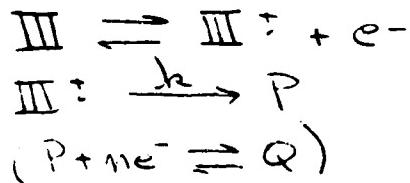
decay.

Whether this decay involves an electron transfer or not, a chemical step is certainly involved; it is the product of this decay which appears at cathodic potentials upon reverse sweep to negative values in the cyclic voltammetry described earlier. Assuming first or pseudo first order kinetic behavior, we can compute the homogeneous rate constant for the decay of the radical cation from the spectroelectrochemical data utilizing the technique described in (12) and (13), where the rate constant

$$k = \frac{[-\Delta R/R]_0 - [-\Delta R/R]_t}{\int_0^t [-\Delta R/R]_t dt}$$

Here  $[-\Delta R/R]_0$  is the change in reflectance which would be obtained at time t if the absorbing species does not decay, and  $[-\Delta R/R]_t$  is the change in reflectance where decay occurs with a first order rate constant k. Computation of this k value was performed from data from various transients in excess of 100ms length, and a mean homogeneous first order rate constant of  $1.99\text{s}^{-1}$  was determined for the degradation of the cation radical.

The data are consistent with the following mechanism for the oxidation of III, either in the presence or absence of oxygen:



It was not possible from the spectroelectrochemical data to determine between an EC or an ECE mechanism, but it is probable that the decay occurs in a fashion

wherein the cation radical undergoes a chemical reaction with trace water, followed by electron transfer.

MSRS spectra for the cation radicals of III and V gave similar wavelengths of maximum absorption: 473 and 480nm respectively. This indicates that the cation radicals have similar ground state electronic energies. The HOMO-LUMO electronic transition energies calculated with the Huckel programs were also consistent with these observations.

#### CONCLUSION

This work supplements earlier electrochemical studies performed on strained systems of this type (5). The voltammetric and spectroelectrochemical studies suggest significant electronic differences in both III and V as well as their respective anion radicals, while indicating that the cation radicals of the two species are energetically similar. Spectral studies on neutral alkylidene cycloproparenes (14) have shown the stability of the cyclopropabenzene derivatives to be less than that of their naphthyl homologs. Simple Huckel molecular orbital calculations gave results which were consistent with these observations. Indeed, strained derivatives of naphthalene are known to be more stable than those of benzene (1). Continued electrochemical investigations upon these and related strained molecules is currently underway, and will be the subject of future reports. Additional studies of the general reaction of oxygen and its electrogenerated ions with organic substrates and their ions is presently underway and will be the subject of forthcoming publications.

**ACKNOWLEDGEMENTS**

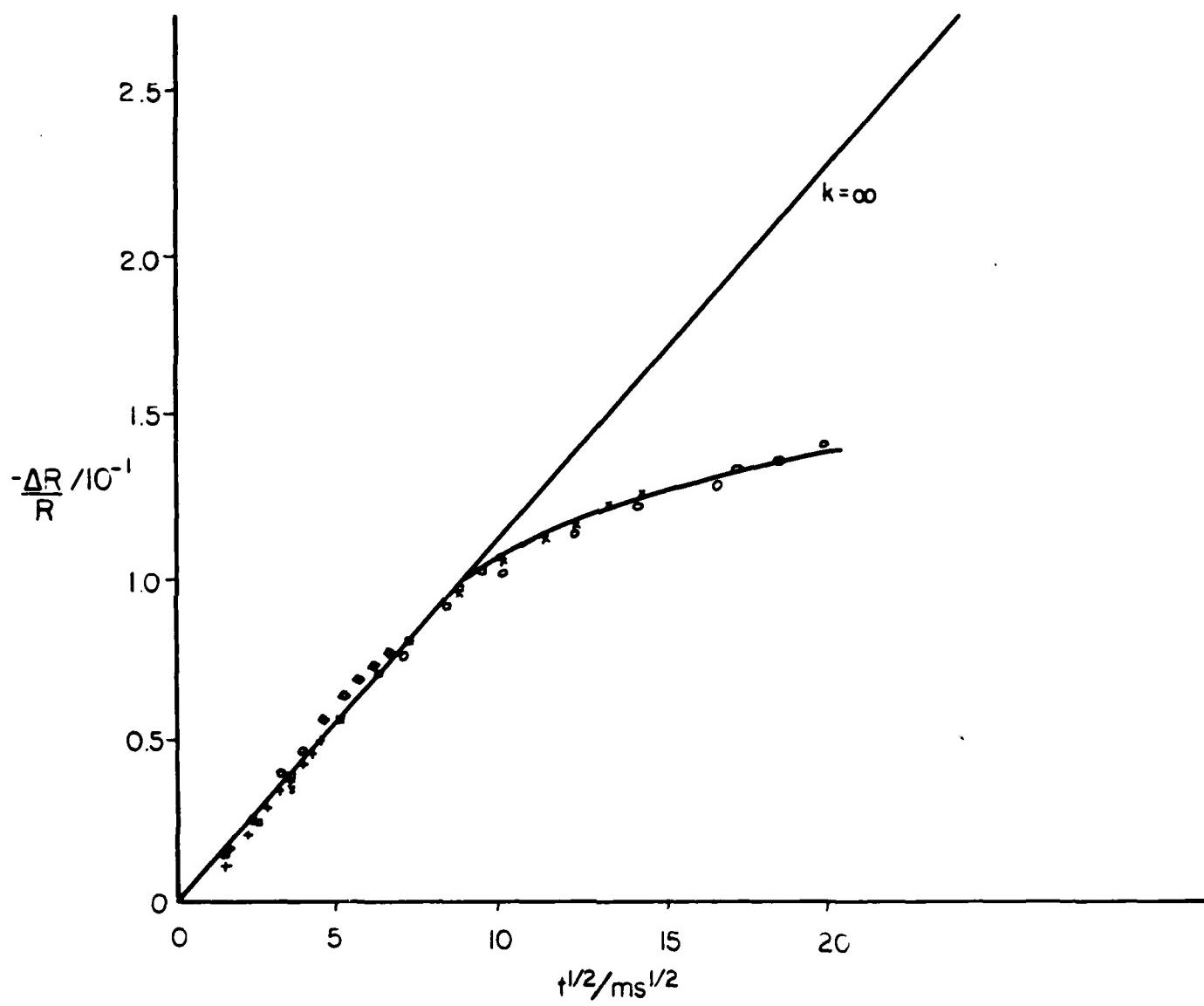
S. P. thanks the Office of Naval Research for support of part of this work. and John Mellor for valuable discussions regarding the electrochemical results. P. J. S. acknowledges the support of the National Science Foundation (CHE84-19099). K. A. thanks Carol Korzeniewski for the use of her Huckel programs.

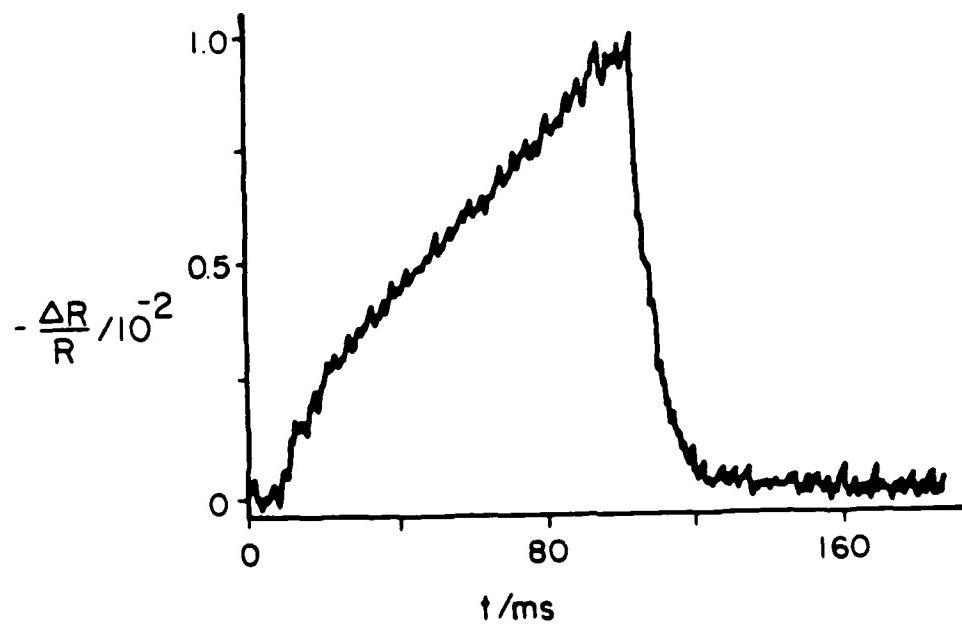
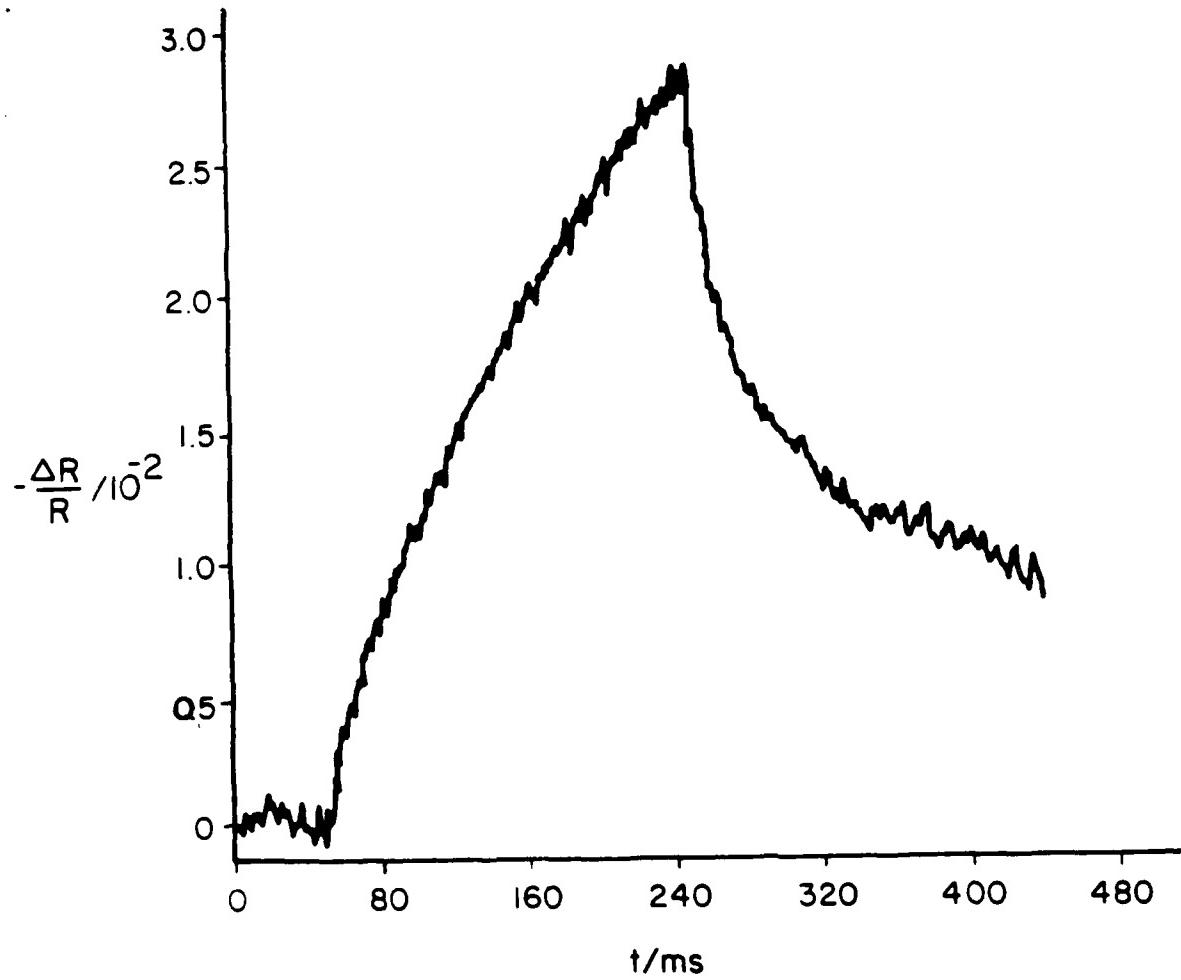
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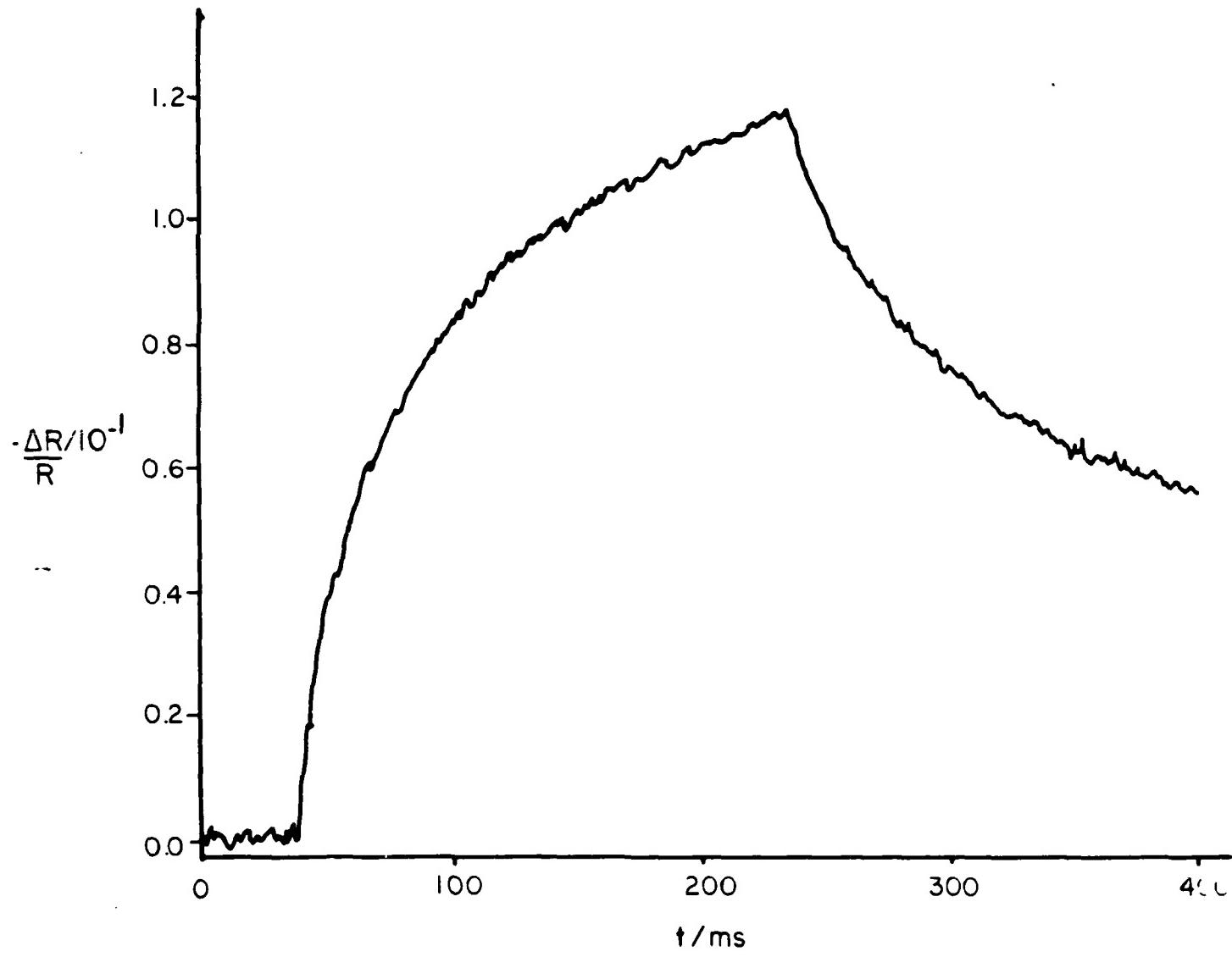
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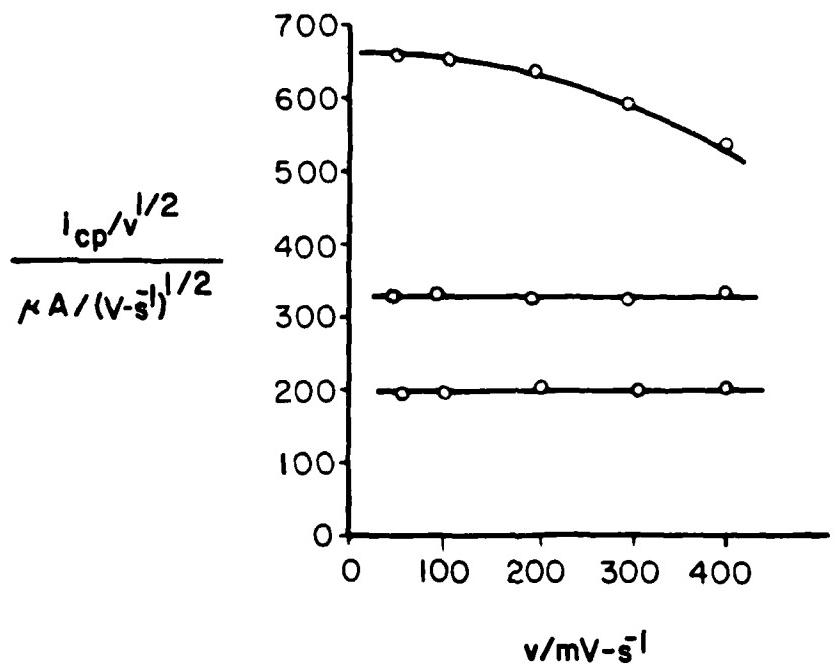
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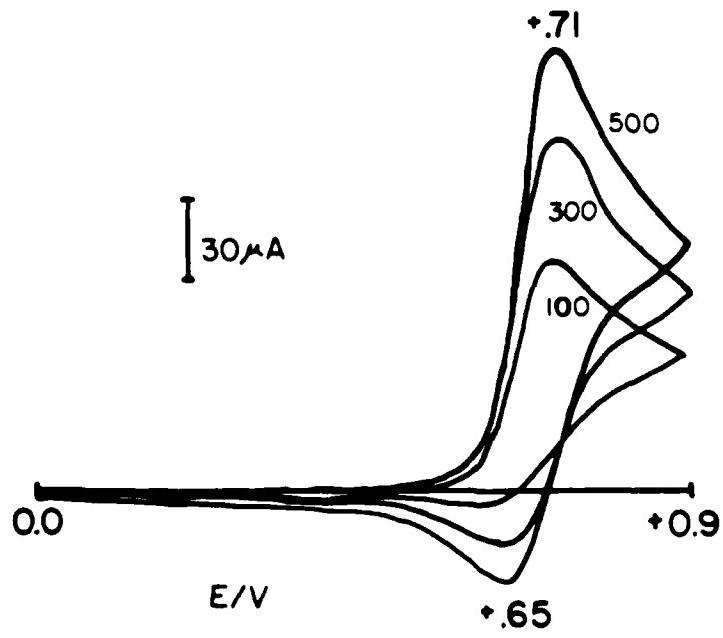
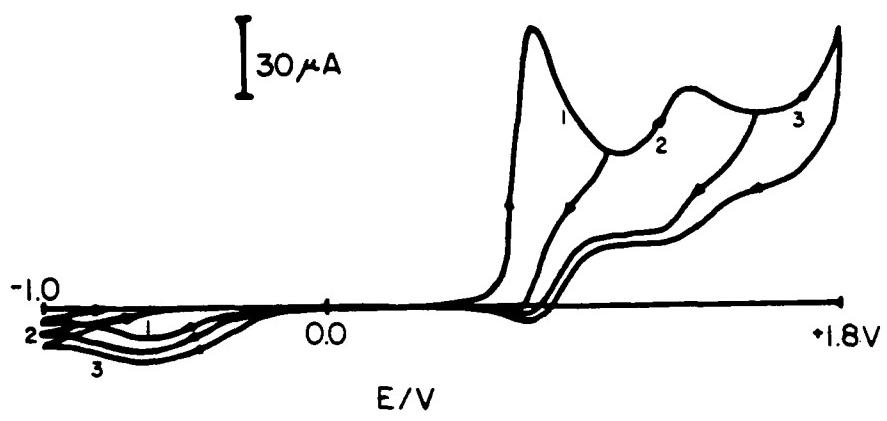
1. Cyclic voltammetry for a) III and for b) dioxygen in 0.15M TBAF / acetonitrile solution at a platinum electrode. The sweep rate was 50mV s<sup>-1</sup>. Potentials are vs. the Ag/Ag<sup>+</sup> (0.01M AgNO<sub>3</sub> in 0.1M TBAF in acetonitrile) reference electrode.
2. Cyclic voltammetry of the mixed system of the components in Figure 1. Parameters the same as in Figure 1.
3. Plots of the normalized peak current vs. sweep rate for the data in Figures 1 and 2. I is that for the reduction peak in Figure 1b; II is that for the reduction peak in Figure 1a; III is for the reduction peak at -2.35V in figure 2. Except for the sweep rate, the parameters are the same as those in Figure 1.
4. Cyclic voltammetry of 1mM III in acetonitrile. Potential program was 0.0V to positive potentials, then reversing to negative potentials, then returning to zero. Parameters the same as in Figure 1.
5. Cyclic voltammetry of 1mM III in acetonitrile as a function of sweep rate. Parameters the same as in Figure 1.
6. Reflectance spectroelectrochemical transient at 587nm for the anion radical of III in the solution described in Figure 1a. (The solution is oxygen free).
7. Reflectance spectroelectrochemical transient at 587nm for the anion radical of III in the solution described in Figure 2. (The solution contains oxygen).
8. Reflectance spectroelectrochemical transient at 473r for the cation radical of III in the solution described in Figure 4.
9. Reflectance vs. square root of time plot for the formation of the cation radical from transients of duration: + 20ms;  $\diamond$  40ms;  $\square$  100ms;  $\times$  200ms;  $\circ$  400ms. Solution is that described in Figure 4.

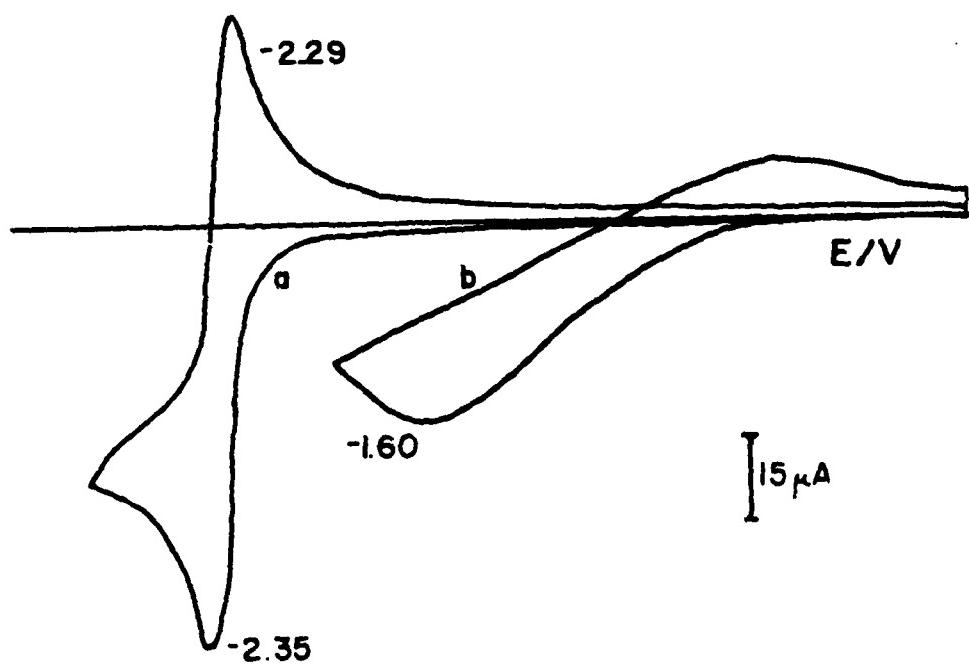


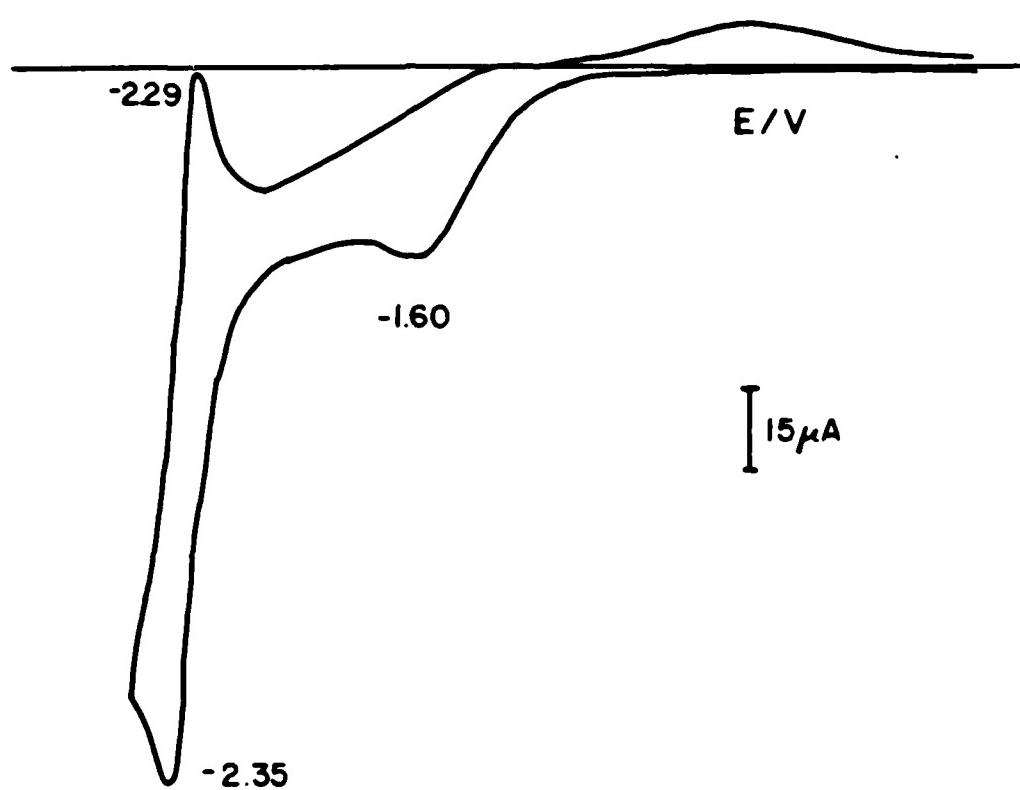












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